



Dendronized metal nanoparticles - self-organizing building blocks for the design of new functional materials

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Final report for the project:

"Dendronized metal nanoparticles - self-organizing building blocks for the design of new functional materials."

Award FA8655-13-1-3001

Recipient principal investigator : Dr. Bertrand Donnio

Abstract

Organizing functional nanometric units in 2D or 3D superlattices is the first steps towards the fabrication of metamaterials with unprecedented optical or magnetic properties. To achieve this goal, we planned the synthesis and structural characterization of various types of mesomorphous hybrid materials of spherical metal nanoparticles functionalized with either polycatenar or dendritic proto-mesogenic ligands, which would be able to self-organize into lamellar, columnar or cubic structures and consequently exhibit original or enhanced (optical, magnetic,...) properties. The fact that our systems are mesomorphous also let envision that they will be addressable, *i.e.* it should be possible to modulate their properties with applied external stimuli, *e.g.* electric fields, temperature. The original goal rapidly produced offsprings: once the synthesis had been done, the structural characterization proved to be a challenge in its own, as did the study of the materials' physical properties. At the date of writing, chemistry is complete, structural characterization is underway, functional characterization has just started.

The hybrids that we have synthesized are based on plasmonic gold and silver nanoparticles (NPs) but the concept is transposable to other metals. The metal NPs have been functionalized with a variety of linear or dendritic ligands which, in particular, induce the mesomorphism. We now have access to a vast and diverse library of nano-hybrids able to self-organize in 2D or 3D, and which, when mixed together, also form binary superlattices. Beyond the physical characterization of these systems we are now pondering their use as metamaterials with innovative optical and/or magnetic properties.

A - Synthesis of the nano-hybrids

Polycatenar mesogens

Most of the studies reported in the literature deal with gold NPs functionalized with classical calamitic mesogens, grafted side-on or end-on. This approach is not always successful and the choice of mesogens is limited. For this project, we have designed polycatenar proto-mesogens comprising a rigid core of two to four aromatic rings (control of the anisotropy), connected to the metal nanoparticle via a flexible spacer. At the other end of the rigid core, two or three aliphatic chains are attached, in order to increase the solubility and decrease the transition temperatures (*cf.* diagram below), as well as to favour self-ordering. Because of the conical shape adopted by these proto-mesogens, we anticipate the formation of micellar cubic liquid-crystalline phases in the bulk, as well as a great diversity of single-components and binary nanoparticle superlattices.

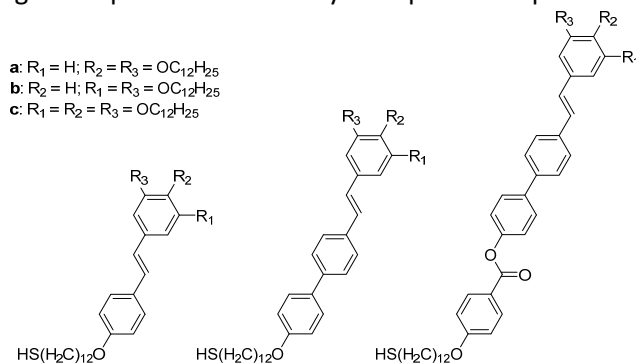


Figure 1. Structures of the polycatenar ligands (**L₂**, **L₃**, and **L₄** for 2, 3 and 4 aromatic rings).

A total of 9 compounds have been synthesized at gram scale and fully characterized (NMR, mass spectrometry, elemental analysis,...). The mesomorphic behaviour of the ungrafted ligands has been evaluated, using DSC (differential scanning calorimetry) and SAXS (small angle X-ray scattering), the behaviour of the nanoparticles grafted with these ligands is underway and will require more time (see below).

Dendritic ligands

The grafting of dendrons onto the surface of nanoparticles is also a promising approach for their subsequent organization in 2D and 3D. It indeed offers specific advantages thanks to the high degree of control that we have on the structures, composition and sizes (generation) of these dendrons. The concept that we have developed is original in that it enables the design of unique molecular architectures, versatile because the choice of dendritic structures is large, and it opens the route to multifunctionality. Upon increasing the dendritic generation, interparticle spacing is very precisely controlled, which means that interparticle interactions also are precisely controlled. Higher generation dendrons also will enable the stabilization of large spherical NPs and of NPs with non-spherical shapes such as rods, cubes, platelets or toruses.

Within the frame of this project, we synthesized a series of dendritic ligands for NPs functionalization, based on a benzylether structure, bearing hydrogenated and fluorinated terminal chains with a variety of substitution patterns, which proportion and assembly are strictly controlled. The dendrons possess an apical alkyne function to allow the attachment of a specific grafting group, namely azide, using "click chemistry".

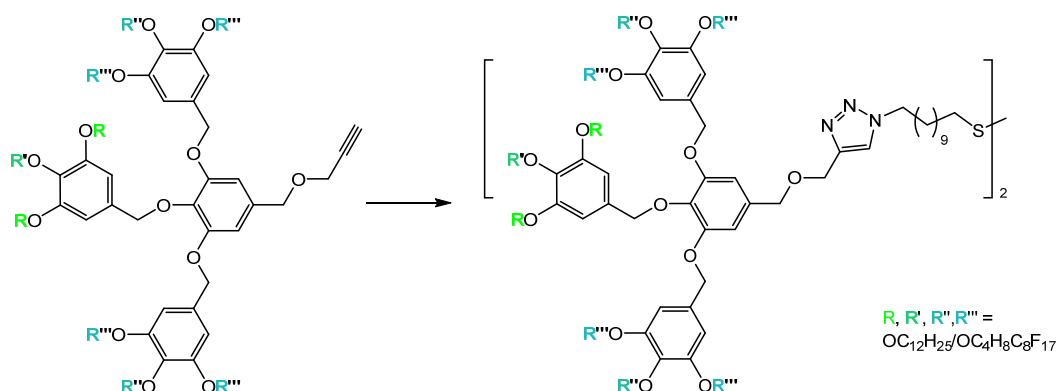


Figure 2. Example of the molecular structure of a dendron. The anchoring (here disulfure) chain will be added on the alkyne group, using click chemistry.

Attaching such dendrons onto NPs yields "patchy" particles because of the nano-segregation occurring at the periphery between hydrogenated and fluorinated chains. This should influence the assembling of the nano-hybrids.

Fluorocarbonated materials elicit an increasing attention because of their exceptional properties as compared to hydrogenocarbonated ones. They boast a very low surface energy, remarkable surface properties, high fluidity, high vapor tension, high compressibility, high gas-solubility, high dielectric constant and refraction index, high hydro- and lipo-phobicity, low viscosity and a high resistance to physical, chemical and biological agents. Up to now fluorinated molecules have very scarcely been used in the field of nanoparticles in spite of their enormous potential. The main reason for this probably is the solubility problems which arise during the course of their synthesis.

We have developed a modular synthesis which gives total control over the number and position of the terminal fluorinated chains. Our strategy also permits at the late stage of the synthesis to adapt the desired type of anchoring function, *e.g.* carboxylic or phosphonic acid, amine, sulfonate, thiol, etc... to bind specifically on various NPs surfaces. To begin, we have synthesized a series of 16 ligands which covers all possible configurations of the chains (Chart 1).

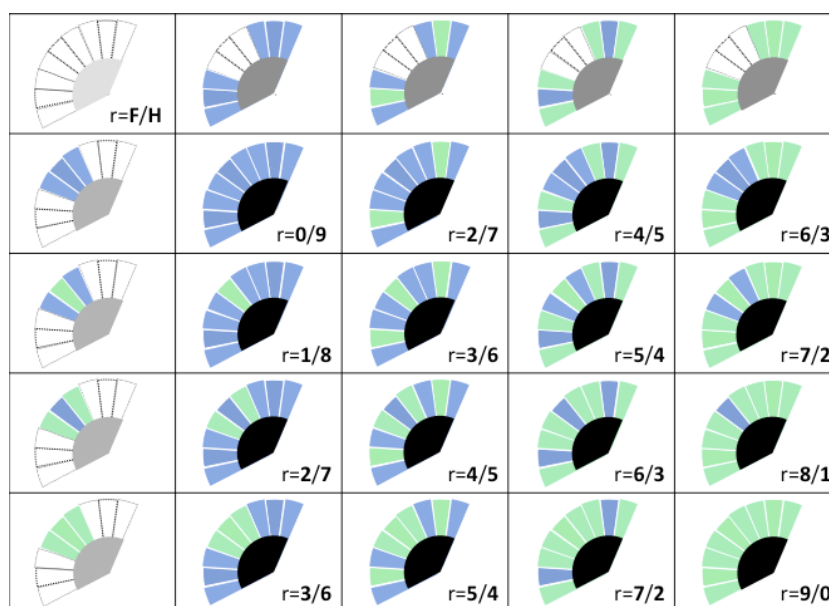


Chart 1. Sum-up of the structures that have been synthesized. r is the ratio of fluorinated (F) chains over hydrogenated chains (H).

Because of the nano-segregation that will take place at the periphery of the dendrons, we expect that the ordering of the nano-hybrids will proceed in ways that differ from the ordering of hybrids bearing only hydrogenated chains. The figure (Figure 3) below illustrates how the "surface" of the nanohybrids could become spatially modulated.

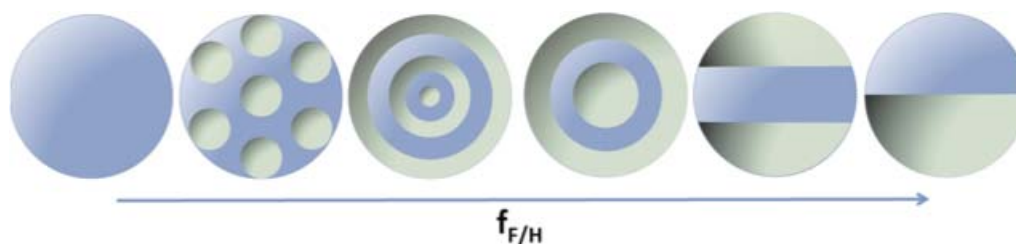


Figure 3. Schematic representations of the NP surface "patchiness" as a function of the the ratio $f_{F/H}$

The whole series of 16 compounds has been synthesized and fully characterized. The intermediate acid forms of the dendrons (*i.e.* a carboxylic acid group replaces the diethylether alcyne group at the apex of the dendrons) have all been tested for mesomorphism (DSC, POM, SAXS). Most of them order in cubic mesophases between room temperature and ca. 100°C, resulting from the aggregation of a finite number of branches into giant micelles, localized at the nodes of a cubic lattice. Complete characterization is underway. Similarly, the ordering behaviour of the nano-hybrids obtained when these dendrons are attached to nanoparticles is just beginning.

B - Structural characterization

The mesomorphic behaviour (or lack thereof) of the materials, *i.e.* the presence of one or several mesophases in the phase diagram is rather easily performed using TGA and DSC. This has been done for all the ligands that have been synthesized, prior to their grafting onto nanoparticles. When needed, structural analysis using small angle X-ray diffraction has been performed on-site. After grafting, the resulting nano-hybrids also have been studied using TGA and DSC.

For those nano-hybrids which are mesomorphous, structural characterization must be performed using physical means such as neutron diffusion and small angle X-ray scattering. Neutron diffusion gives information on the organic ligand shell (thickness, ordering, ...) whereas X-ray diffusion gives

information on the metal cores and on the superlattices. As these cores very much absorb X-rays and given the characteristic lengths of the elementary cells, X-ray studies have to be performed at synchrotron light sources.

The systems that we have synthesized are able to self-organize in 3D but also in 2D, as checked on TEM grids. Moreover, the rational mixing of 2 species can also give rise to binary lattices. We shall describe hereafter the preliminary results that we have already obtained with single and binary systems.

a) Single-component systems

We have started studying the organisation properties of Au nanoparticles ($\varnothing = 7$ nm) grafted with polycatenar ligands. The efficient grafting is ascertained with TGA analyses and is even obvious on TEM (transmission electron microscopy) images, as it can be seen that the interparticle distances increase with the number of aromatic rings in the rigid core (See Figure 1, from 2 (L_{2b}) to 4 (L_{4b}) aromatic rings, with substitution pattern type **b**).

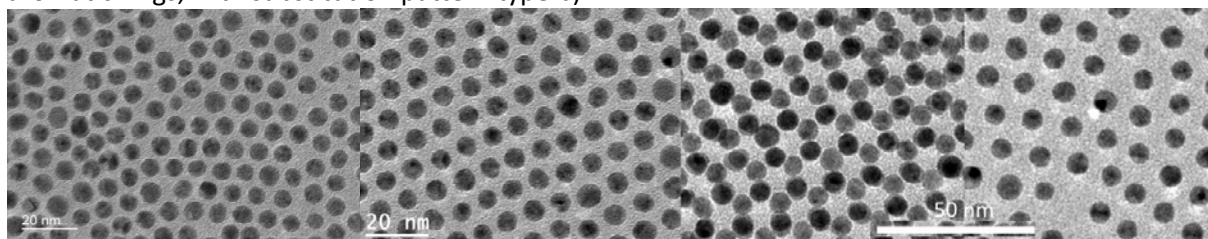


Figure 4. TEM images of the hybrids $Au@OAm \rightarrow Au@L_{2b} \rightarrow Au@L_{3b} \rightarrow Au@L_{4b}$ ($\varphi_{Au} \approx 7$ nm). Note the absence of order for the oleylamine-coated NPs (1st image), and the increase of the interparticular spacing..

SAXS measurements suggest that the hybrids organize in *fcc* cubic phases between room temperature and *ca.* 120 to 140°C, where they transit to an isotropic phase. This transition seems to be reversible and the cubic phase reappears and persists down to RT (Figure 5). For example, for nano-hybrid $Au_{6-7nm}@L_{2b}$ this symmetry is that of the compact packing of identical spheres. The space between NPs is filled by the organic part, most probably in isotropic form. The nano-hybrid therefore adopts a polyhedral volume to fill the space between the inorganic cores, or more precisely a rhombo-dodecaedral shape, in order to pack efficiently in the *fcc* lattice. This cubic structure naturally emerges from the long range-correlated piling-up of monolayers with hexagonal packing (TEM) : there is the most perfect identity between the a_{2D} parameter of the cubic sub-cell and a_H , measure on a TEM image showing 2 superimposed hexagonal lattices. Each new layer shifts with regards to the preceding one (regular alternation of A-B-C layers).

These preliminary studies are very promising since they demonstrate that the grafting of a simple polycatenar ligand, non mesomorphous, with symmetrically substituted terminal chains, drives NPs to order with control interparticular spacings, differently in 2D and 3D, than NPs coated with "passive" ligands. We also observed the evolution of these arrangements (2D and 3D) as a function of the ligands' anisotropy (Figure 1, $L_2 \rightarrow L_3 \rightarrow L_4$), as just evoked, but also of the chains' substitution pattern on the ligands (Figure 1, **a** \rightarrow **b** \rightarrow **c**). It appears from preliminary conclusions, that the ideal system bears 3 aromatic rings, and the substitution pattern type **b**. Strangely, despite the increase of the anisotropy, the stability of the corresponding hybrid ($Au@L_4$) is lesser than that of ($Au@L_3$), hybrid ($Au@L_2$) being just amorphous, and that the increase of the chain volume is also prejudicial to mesomorphism. Structural characterization of the systems we have synthesized is ongoing.

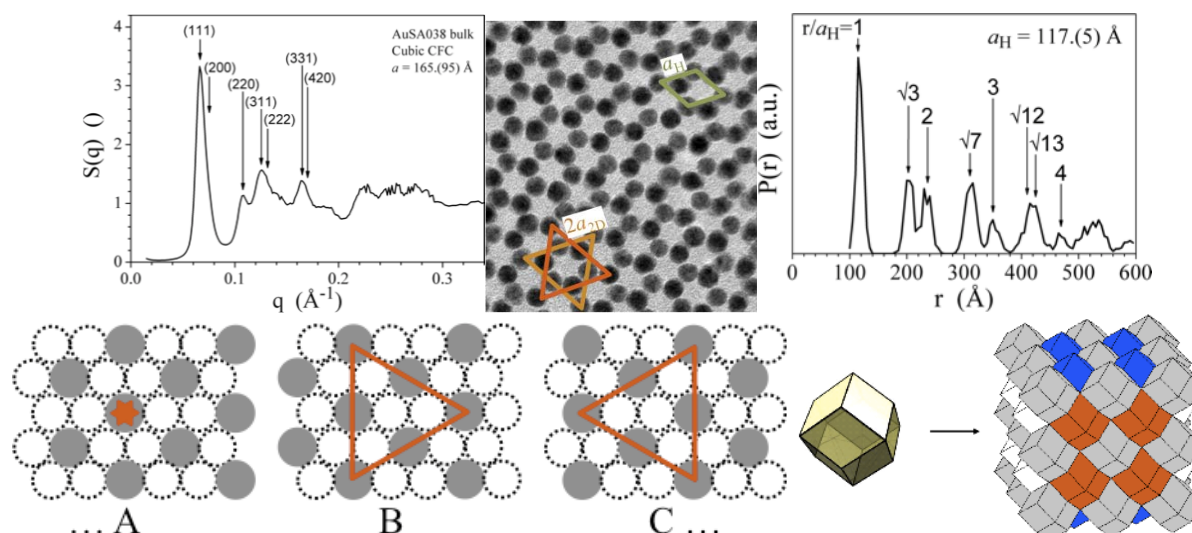


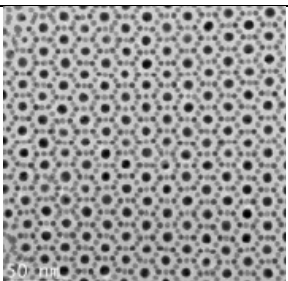
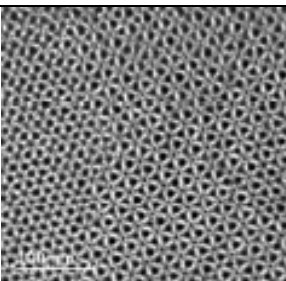
Figure 5. SAXS pattern of the *fcc* cubic phase of sample $\text{Au}_{6-7\text{nm}}@L_{2b}$, and TEM image (together with TEM image analysis). Symmetry of the cubic phase is $Fm\bar{3}m$, there are 4 nano-hybrids per unit cell ; fundamental domain of the *fcc* lattice is a rhombic dodecahedron.

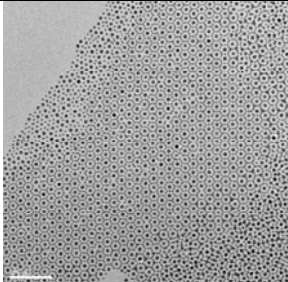
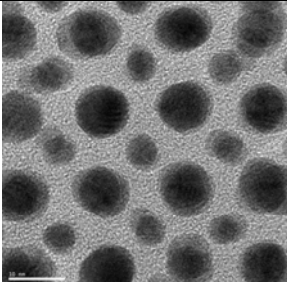
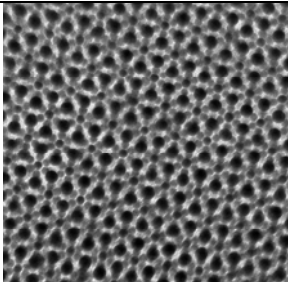
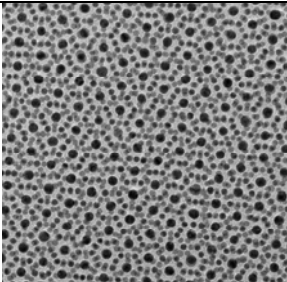
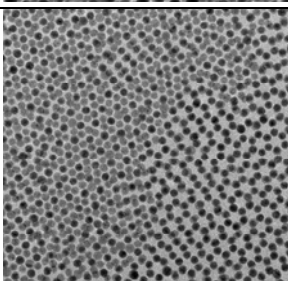
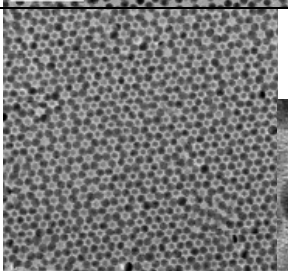
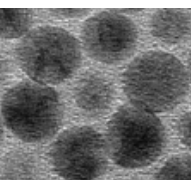
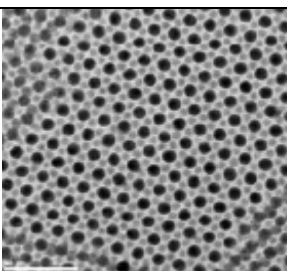
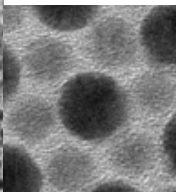
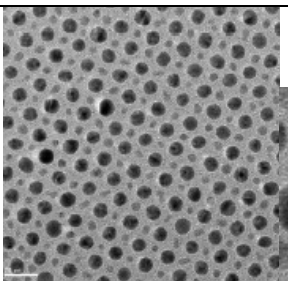
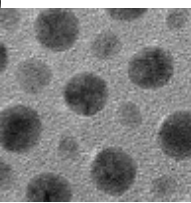
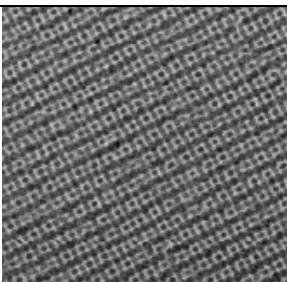
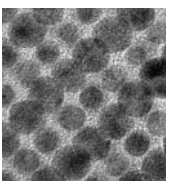
Understanding and controlling these materials nevertheless require that we deepen our knowledge of these structures. As we have just seen, grafting an organic shell induces a mesophase right from room temperature, and regular patterns simultaneously appear in the TEM images. SAXS measurements on solutions and in bulk samples provide access to form and structure factors of the hybrids, from which we get a better understanding of nanoparticles lattices. Nevertheless, because of the high electron density of gold and the relatively large size of the cores, the organic coating appears as transparent or un-structured in volume. A crucial part of the structure is consequently beyond reach of X-rays since the mesomorphism stems from a nano-segregation process between incompatible segments within the organic shell. Contrary to that, small angle neutron scattering (SANS) is an ideal method for completing such studies since there, density contrast is highest between aliphatic and aromatic segments of the organic shell, with gold lying in-between. Combination of SAXS and SANS data will allow to resolve the entire structure of the hybrid material and to better understand these systems. Some SANS data have already been acquired and we are engaged in the analysis process.

b) Binary systems

One of the many advantages of our systems is that the nano-hybrids are intercompatible, that is they can be mixed in arbitrary proportions. We have started screening which nano-hybrids form ordered lattices when mixed together. We start with core made of Au or Ag for the ease of synthesis and analysis but basically any core could be substituted to the present ones. A selection of images is given below.

Table 1. Selection of binary lattices (TEM grids)

Super-réseaux binaires		
$\text{Au}_{8.7\text{nm}}@L_{2b}$ + $\text{Au}_{5.9\text{nm}}@L_{2b}$ in varying proportions	 CaCu5	 MgZn2

$\text{Au}_{8.7\text{nm}}@L_{2b}$ + $\text{Au}_{5.9\text{nm}}@L_{3b}$ ratios 1:2 & 1:1.5	 CaCu5	 CuCl
$\text{Au}_{8.7\text{nm}}@L_{3b}$ + $\text{Au}_{5.9\text{nm}}@L_{2b}$ ratios 1:2 & 1:4	 MgZn2	 CaCu5
$\text{Au}_{5.9\text{nm}}@L_{2b}$ + $\text{Au}_{5.6\text{nm}}@L_{3b}$ ratio 1:1		
$\text{Au}_{8.5\text{nm}}@L_{2b}$ + $\text{Ag}_{5.9\text{nm}}@DDT$ ratios 1:1 & 1:2	 	 
$\text{Au}_{8.5\text{nm}}@L_{2b}$ + $\text{Ag}_{5.9\text{nm}}@DDT$ ratios 1:2 & 1:4	 	 

We are just starting to explore which mixtures successfully order in binary lattices with long range order. These systems look very promising for the development of metamaterials. Still, their characterization is a challenge, especially when it comes to 3D samples.

C - Functional characterization

The isolated NPs possess optical and magnetic properties, we expect that synergetic interactions, resulting from the "supramolecular" ordering will develop, as it has already been observed in similar (non-mesomorphic) systems. From these interactions the material will exhibit new or enhanced

properties such as ex nihilo magnetism, collective plasmon resonances, etc. We have recently suggested that the magnetism of Au NPs stems from persistent currents, this particular point will be specifically investigated, with the synthesis of new ferromagnetic materials in mind.

Another ambitious point will be to try modulating the optical or magnetic response of NP assemblies with an external electric field. It is well known that some liquid-crystalline phases (e.g. nematic) are easily controlled in this way. This would pave the way to an electrically controllable metamaterial.

We have initiated several on-site and off-site collaborations with optics physicists in order to start assessing the optical properties of our assemblies.

At least four papers are in preparation.